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(54) **High wear-resistant member, method of producing the same, and valve gear using the same for use in internal combustion engine.**

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(56) References cited:  
**WO-A-84/04760 FR-A- 2 161 645**  
**GB-A- 864 495 GB-A- 1 119 516**  
**GB-A- 1 287 937 GB-A- 1 316 249**  
**US-A- 3 698 877**

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**Description**

The present invention relates generally to a wear-resistant metal member and a method of producing the same, as well as a valve gear using the same for use in an internal combustion engine. More particularly, the present invention relates to a composite member including a wear-resistant material suitable for use in forming sliding members subjected to high loads or impact loads.

In the field of structural components, it is generally unnecessary to ensure that the whole of each structural component is provided with certain properties required for specific purposes. In a typical case, the greater part of a structural component is composed of a relatively inexpensive material, but a specific portion of the surface of the structural component requires particular properties. For instance, a cutting tool is normally constituted by a combination of a hard cutting portion and a remaining portion made of a material which is strong enough not to be deformed or broken by the cutting load. In addition, as the size of such a component increases, a proportion of the part in the component occupied by the portion requiring specific properties is often relatively reduced. It is therefore advantageous, in terms of performance and price, to form such a component by a combination of a base material occupying the greater part of the component and a surface layer made of a material having desired properties. In particular, composite members comprised of a base material coated with a hard surface layer are employed as sliding components of the type which requires a certain level of wear resistance.

Such a composite member for use as a sliding component is described, for example, in Japanese Patent Publication No. 12424/85 which discloses a composite member comprised of a base material which is plasma-sprayed with a powder of high carbon - high Cr cast steel or a mixture of that powder and a powdered self-fluxing alloy. Further, Japanese Patent Publication No. 12425/85 discloses a composite sliding member comprised of a base material which is plasma-sprayed with a powder of high carbon - high Cr cast steel and a powder of Cu alloy. In the process of manufacturing either of these prior-art composite members, however, plasma spraying is effected under atmospheric pressure conditions. Accordingly, it is impossible to achieve satisfactory adhesion of the sprayed material to the base material, as well as a sufficient adhesion strength between individual layers of particles contained in the resultant coating. In addition, no investigation has been made on the density of precipitated hard intermetallic compounds and the degree of dispersion thereof.

Further, Japanese Patent Publication No. 57552/82 discloses a method of using CVD to coat a base material with a layer of a precipitated hard metal alloy composed of a metal halide and carbon, boron or silicon. This method utilizing CVD, however, involves problem in that the strength of adhesion between the base material and the layer or the toughness of the precipitated layer is reduced owing to treatment strains caused by differences in physical values between the base material and the layer coated thereon, since the precipitated layer is present in a single phase. The above Publication further discloses that only the precipitated layer is utilized by taking out it. However, as the size of the precipitated layer increases, it becomes impossible to achieve a sufficient toughness, owing to the fact that the precipitated layer is an intermetallic compound. Also, since heat decomposition of the metal halide is utilized to form the precipitated layer on the base material, the treatment cost per unit area increases due to various factors such as the high production cost of the metal halide and the necessity for post-treatment of a halogenating gas. This limits the kind of components to which this prior art method is applicable.

On the other hand, for a high hardness material (ingot) made by melting, an alloy disclosed in Japanese Patent Publication No. 17069/82 is known as a wear-resistant cutting tool steel. As the content of MC-system carbide is increased, the wear resistance of this alloy is improved. However, if the V content is increased in order to increase the MC-system carbide content, the melting temperature of this alloy rises, thereby making it difficult to produce the alloy. In addition, the specific gravity of the MC-system carbide is lower than that of the melt, so that the MC-system carbide tends to move upward during melting, and this hinders the production of a homogeneous metal structure. Moreover, as the melting temperature rises, the particle size of carbide becomes larger during the crystallization thereof, thereby causing reductions in toughness and in machinability. Therefore, in a melting method, the composition range of the alloy is determined by the conditions governing working, not by the properties of a product, thereby reducing the range of machine design.

It is known that valve gear incorporated in an internal combustion engine has various sliding surfaces which are maintained in sliding contact with each other, and the sliding surfaces thereof are made of alloy steel or case-hardened steel which is subjected to surface hardening by means of heat treatment. In this case, a thick hardened layer or a hard sintered material is embedded in a portion of a cam shaft which is in contact with a cam wheel, since that portion requires an extremely high wear resistance. For example, Japanese Patent Application Laid-Open Publication No. 53612/83 discloses a structure in which a Co-based

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sintered alloy containing carbide is bonded, at the surface of a tappet contacting with a cam, to a body of the tappet made of steel or cast iron through an intermediate layer consisting of Fe-based sintered alloy which was sintered in liquid phase. The valve lifter (called "tappet" in the above Laid-Open Publication) possesses a very good wear resistance, such as scuffing resistance, etc. However, in the production of the structure, the Co-based alloy powder to be become a surface layer is compacted and then the Fe-based alloy powder to be sintered in liquid phase is compacted thereon, and thereafter they are attached to the body of the valve lifter. Then, the thus-assembled body is heated to a temperature at which the Fe-based sintered alloy becomes liquid phase. Accordingly, in this production process no satisfactory considerations are given to a productivity, a deformation caused by the heating to high temperatures, and an increase in the price incurred by the use of expensive materials such as Co.

On the other hand, Japanese Patent Application Laid-Open Publication No. 214609/83 discloses a valve lifter in which a reduction in the weight is taken into consideration. According to the art disclosed in this Laid-Open Publication the body of the valve lifter is produced from a casting of aluminum, magnesium or other light alloys, and the sliding portion of its surface which is brought into contact with a cam wheel is sprayed with ceramics, tungsten carbide or the like. Accordingly, a reduction in the weight of the body is achieved to some extent, but the wear resistance and the durability of the surface are not sufficiently taken into consideration. In a typical spraying method, particles having a particle size of several  $\mu\text{m}$  to several hundreds  $\mu\text{m}$  are sprayed onto a base material to form a coating thereon. Accordingly, the bonding strength between the coating and the base material is achieved mechanically, and the strength thereof will be several  $\text{kg/mm}^2$  at best. Also, the interior of the coating exhibits a laminated structure containing a multiplicity of pores, and thus the bonding strength between individual layers formed by the sprayed particles is weak. Therefore, the phenomenon of pitting may take place under conditions of high-load friction. In addition, the body does not have a sufficient toughness since it is formed from a light alloy casting.

A primary object of the present invention is to provide a wear-resistant member containing a homogeneously distributed, fine compound having a very good wear resistance and a method of producing the same, as well as a valve gear using the same for use in an internal combustion engine.

The present invention resides in a wear-resistant metal member as set out in claim 1.

In accordance with the invention, the areal ratio of the carbide or carbonitride particles ranges from 25 to 90%, and preferably these particles are formed mainly in such a state that numerous particles are bonded together, thereby providing a high wear resistance.

The present invention also resides in a method of producing a wear-resistant metal member, as set out in claim 6.

The method of the present invention may further include the step of effecting a carburizing, nitriding or carbonitriding treatment prior to the aforesaid hardening treatment and the step of effecting a plastic working prior to the carburizing, nitriding or carbonitriding treatment.

The present invention further resides in a wear-resistant sliding mechanism comprising metal members which are maintained in sliding contact with each other, at least one of the metal members being as claimed in claim 1 or made by a method as claimed in claim 6.

The present invention resides in a valve gear for use in an internal combustion engine, as set out in claim 11. The metal members may include a valve lifter, having a carbon content in the range 0.1 to 0.4%.

By the invention, it is possible to obtain structural members which are reduced in size but excel in toughness, pitting resistance, scuffing resistance and wear resistance.

In general, in order to improve the load resistance and wear resistance of a sliding member, it is desirable that the surface layer of the sliding member has a structure in which a matrix phase having high toughness and a hard phase are firmly bonded together and, in addition, in which the hard compound is fine and its areal ratio is large. Accordingly, it is desirable that a large amount of a fine compound, such as a carbide, a nitride or a carbonitride, is crystallized in a surface layer, that is, the hard coating. However, if the amount of carbon added is raised to increase the carbide content, the melting temperature of the material rises, the carbide becomes coarse, and further segregation or the like occurs owing to difference in the specific gravity, thereby reducing the wear resistance and load resistance.

The above-described problems are solved by the wear-resistant member of the present invention. In the present invention, with respect to the fragmentary hard compound, its size in width is limited to 3  $\mu\text{m}$  or less and its areal ratio to 25 to 90%. The reason therefor will be described below. In general, if fragmentary hard compounds having a widthwise size of 3  $\mu\text{m}$  or greater occupy the greater part of the structure of the wear-resistant member, the surface area of each of the compounds responsible for bonding is reduced when the compounds have a complicated shape, as in the case of the fragmentary compounds of the present invention, so that the bonding between the hard compounds and the matrix phase becomes

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insufficient. Accordingly, if such a member is employed as a high hardness member, the compounds easily exfoliate during finishing or use. Also, if each of the compounds has a widthwise size of 3  $\mu\text{m}$  or greater with an areal ratio of 25% or less, the area of the matrix which is softer than the compound increases. As a result, cracks occur owing to the deformation of the matrix, or the compounds partially exfoliate or drop owing to the wear in the surrounding phase, so that the wear resistance of the member is reduced. In particular, the compounds exfoliated during use get caught in the clearance between surfaces of components which are maintained in frictional contact with each other, thereby scuffing the surfaces. Alternatively, the exfoliated compounds act as an abrasive and thus accelerate the wear.

It is to be noted that the nitride and the carbonitride can be produced by forming a sprayed layer in a reduced pressure atmosphere.

The following is a description of the composition of the surface layer.

Carbon is a primary component which combines with other elements to form a simple or composite carbide to improve wear resistance, and is intimately associated with carbide formers. As the amount of the carbide formers added is increased, the content of hard carbide can be increased. When the amount of the carbon added is 2% or less, it becomes impossible to obtain satisfactory wear resistance which is indispensable for a high hardness member. As the content of carbon is increased, the amount of the carbide that is crystallized increases to improve the hardness of the surface layer. However, if the amount of the carbon added is 10% or greater, free carbon appears and this causes the workability during melting, hot working, cold working, grinding or the like to be lowered and, in addition, the hard layer becomes brittle since pores are produced therein. In terms of hardness, spraying workability, toughness and so forth, the amount of the carbon to be added is preferably 2.5 to 5%, more preferably 2.5 to 3.5%. It is desirable that 80% of the content of the carbon forms a carbide. When carbon exists in solid solution state or graphite, wear resistance is significantly reduced and the brittleness of a coating remarkably increases. Also, the content of oxygen in the coating is an important factor in terms of the coating's toughness. As the oxygen content increases, an oxide precipitates to make the coating brittle. The critical value of the oxygen content is about 1500 ppm and, when this value is exceeded, the toughness is significantly reduced to cause the phenomenon of pitting. Also, it is desirable that the coating and the base material are bonded together by forming a diffused layer therebetween in order to achieve a sufficient durability. The thickness of the coating is also important for durability and reliability. For example, if the coating thickness is less than 0.2 mm, the wear resistance of the coating is reduced under the influence of the base material when exposed to friction under high-load conditions, and further after the coating has become worn the degree of wear increases. In order to improve the toughness of the coating, it is desirable that fine carbide is uniformly distributed. More preferably, the content of carbon and the amount of distributed carbide should increase toward the surface of the coating.

Cr is an element which forms a carbide and improves the ability to heat-treat the matrix, wear resistance and load resistance, and which has a specific gravity smaller than the matrix metal and is economically advantageous. If the amount of Cr added is less than 18%, it is impossible to obtain a satisfactory effect, although its effectiveness may of course depend upon other components which coexist with Cr. As the Cr content increases, the hardenability increases. However, if the Cr content exceeds 60%, workability is greatly reduced and it thus becomes difficult to form a homogeneous layer and thus the hard layer becomes embrittled owing to the pores produced therein. In particular, the amount of Cr added is preferably 25 to 35% from the viewpoint of homogeneous distribution of carbide, spraying workability and toughness.

V is a significantly effective component since it forms a carbide and acts to finely divide and toughen the crystal grains of a matrix. In general, a carbide containing V is extremely hard, and a slight amount of V can produce a satisfactory effect in finely dividing the crystal grains and in hardening by nitriding. However, in the case of high alloy steel system as in the present invention, when the V content is 0.3% or greater a significant effect is achieved. As the V content increases, the content of a carbide increases so that wear resistance increases. The upper limit of the V content is 20% since the effect of V is saturated at about 20%. Nb and Ta are known as elements of the same group, and they are also effective in forming a carbide, a nitride and a carbonitride to harden the crystal grains, thereby improving the wear resistance. A slight amount of either of Nb and Ta produces a satisfactory effect upon diffusion heat treatment, and the effect of each of them is saturated at 15%. In particular, the amount of either of Nb and Ta is preferably 3 to 11% in terms of homogeneous distribution of carbide, improved hardness of matrix, spraying workability and toughness.

Mo and W form  $M_6C$  and  $MC$  type carbides to improve wear resistance. As the amount of either of these elements added increases, the amount of carbide increases and thus wear resistance is improved. When the amount of either of Mo and W reaches 25%, the effect thereof is saturated. In particular, the

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amount of either of Mo and W is preferably 3 to 10% in terms of homogeneous distribution of carbide, spraying workability and toughness.

Ti, Zr, and Hf of the 4A group act as carbide former or nitride former, and are components effective for hardening. As the amount of each of them added is increased, the effect for hardening is improved. However, when the amount to be added exceeds 10%, workability is reduced, and the surface layer tends to become brittle. In particular, the amount of each of them is preferably 0.5 to 3% in terms of homogeneous distribution of carbide, spraying workability and toughness since these elements strongly act as carbide formers.

In addition, Si and Mn may respectively be contained as a deoxidizer in the amount of 2% or less.

Fe becomes a matrix and forms a martensite-phase matrix to improve the wear resistance. Fe is therefor added in the amount of 20% or greater. Since the wear resistance is obtained by hard substance such as carbide particles, nitride particles or carbonitride particles, it is necessary that the matrix contains these particles in large amounts. Accordingly, in order to obtain a high wear resistance, the Fe content is preferably 70% or less, more preferably 40 to 60%.

The thickness of a hard coating serving as a surface layer is preferably 30  $\mu\text{m}$  or greater. A hard coating having a thickness of less than 30  $\mu\text{m}$  exfoliates during finishing or use, and when it is used under high-load conditions its withstanding pressure is reduced and thus causes deformation of the base material.

In order to form the surface layer serving as the above-described hard coating on the surface of the base material, a melt of the alloy having the composition of the surface layer is atomized and sprayed directly onto the base material, or it is once powdered and the powder is sprayed onto the base material to form a coating. In either case, the surface layer is formed in a reduced pressure atmosphere. For example, if the spraying is carried out in the atmosphere in the same manner as in the prior art, a sprayed powder which is heated by a heating source reacts with an oxygen or nitrogen gas in the air to form a reaction product. Before the reaction product adheres to the base material, the reaction product solidifies or the temperature thereof approaches its solidification point since the reaction product has a high melting temperature. When a coating serving as the surface layer is formed under these conditions, the particles of the powder used are flatly crushed by an impact caused when the powder adheres to the base material, and the thus-crushed particles are superimposed in layers within the coating. Thus, the coating includes a layer containing superimposed particles between which undesired defects are present such as pores and oxides. Therefore, the coating becomes very brittle. To prevent the formation of such a coating, plasma spraying is performed in a reduced pressure atmosphere. In accordance with this plasma spraying, no defects such as oxide films or pores are formed between individual particles, so that adjacent particles fuse together and precipitate as fine compounds, thereby forming a dense hard layer.

It is preferable that the above-described spraying in reduced pressure is performed in a non-oxidizing gas and under a reduced pressure of 13 kPa (100 Torr) or less. Ar, He, H<sub>2</sub>, N<sub>2</sub> and so forth may be employed as the atmosphere. However, in the as-sprayed state, since the diffusion between adjacent individual particles in the coating as well as between the base material and the coating is insufficient, the mechanical strength of the coating is low. For this reason, in accordance with the invention, a mutual diffusion at a boundary between the surface layer and the base material is carried out by a heat treatment to thereby realize high strength and toughness. If this heat treatment is carried out in at least one of carburizing, nitriding and carbonitriding atmospheres, it is possible to more certainly and rapidly effect the mutual diffusion of atoms between adjacent particles as well as between the coating and the base material, and to remove, by the diffusion of atoms from the atmosphere, the impurities between particles which are flatly adhered to the base material as well as to form fine compound which hardens the coating. In consequence, no local wear occurs and a high wear resistance can be achieved over the whole of the coating. In addition, in order to improve toughness, it is also effective to carry out plastic working as required prior to heat treatment. In this case, if a working ratio is 30% or greater in terms of reduction of area, a remarkable effect is achieved. Incidentally, although the base material is softened by spraying, it can be hardened by carburizing and nitriding.

It is to be noted that, as the amount of carbon added is increased in order to increase the content of a carbide or the like, the temperature at which a material is melted rises and further the carbide grows coarsely. It becomes therefore difficult to effectively produce a homogeneous material. A desirable method of solving this problem is as follows. In the state of a material, the carbon content is limited to some extent and the structure of the material is prepared such as to contain large amounts of elements having a low level of free energy for forming a carbide, a nitride and a boride, and after the material has been formed into a constituent part, at least one of carbon, nitrogen and boron is diffused into the surface of the constituent part to precipitate a compound thereof.

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It is to be noted that, after plasma spraying, the surface layer is spontaneously quenched, with the result that a supersaturated solid solution phase increases owing to the effect of quenching. Accordingly, a fine compound is precipitated by a subsequent heat treatment. After the heat treatment, the surface layer is toughened with a high hardness in a quenching-tempering step. Also, the amount of precipitates can be controlled by controlling the composition of materials, the temperature of heat treatment and the amount and ratio of atoms to be diffused.

In accordance with the present invention, unlike prior art melting and sintering methods, owing to the facts that the components having a low level of free energy for forming a carbide, a nitride or a carbonitride exist in a solid solution state in the surface of a base material made of a material having a high toughness and further that a material for forming a carbide is plasma-sprayed onto the surface in a reduced pressure atmosphere followed by heat treatment, it is possible to obtain a very tough composite material which is excellent in wear resistance and has an extremely hard surface layer with a very fine and homogeneous phase and in which the adhesion between the surface layer and the base material as well as the adhesion between the particles in the surface layer are excellent.

Such a surface layer may be formed only in a required area of the base-material surface by spraying. In a case where a wear-resistant material is produced by a production process employing a conventional melting method, the rate at which the material is cooled during forging is limited when the forged material reaches a certain size, so that the precipitated phase becomes coarsened owing to the thermal equilibrium during this cooling, thereby determining the composition range of the material. On the other hand, in the present invention, since the wear-resistant phase is formed using powders having a particle size of 44  $\mu\text{m}$  at the maximum and it is rapidly quenched, it is possible to significantly widen the design range of the material.

- Fig. 1 is a micrograph showing the metal structure, in cross section, of the member according to an embodiment of the present invention;
- Fig. 2 is an electron micrograph showing the metal structure, in cross section, of the member according to an embodiment of the present invention;
- Figs. 3 and 4 are graphs each showing the comparison of the wear losses of samples which were subjected to sliding wear tests;
- Fig. 5 is a cross-sectional view of the essential portion of a valve lifter and a portion of an internal combustion engine;
- Fig. 6 is a micrograph showing on an enlarged scale the essential portion of a portion formed by spraying in a reduced pressure atmosphere;
- Fig. 7 is a graph showing the comparison of the hardnesses realized by spraying in a reduced pressure atmosphere and spraying in the atmosphere;
- Fig. 8 is a fragmentary front elevation, in cross section, of a valve gear according to another embodiment of the present invention; and
- Fig. 9 is a fragmentary front elevation, in cross section, of a valve gear according to still another embodiment of the present invention.

40 Example 1

An alloy steel having the composition (wt. %) shown in Table 1 was melted, and from the melt a powder having a particle size of 10 to 44  $\mu\text{m}$  was prepared by a vacuum atomizing method. The thus-prepared powder was plasma-sprayed in a reduced pressure atmosphere to a thickness of about 30  $\mu\text{m}$  onto the surface of a base material preheated to about 500 °C, the base material being SCM 415 steel (0.4% C - 1% Cr - 0.25% Mo steel). The atmosphere used was Ar under a reduced pressure of 6.5 kPa (50 Torr). The plasma gas used was a mixture of Ar and H<sub>2</sub>, and the plasma current used was 800 A. The temperature of the base material during spraying was about 800 to 900 °C, and the period of spraying was about 10 minutes. Subsequently, the thus-treated material was heated at 930 °C for 30 minutes followed by oil-quenching, and was then tempered at 170 °C for 120 minutes. The conditions of such quenching and tempering were suitable for the heat treatment of the alloy base material. In this manner, Samples A to J shown in Table 1 were prepared. In Table 1, Samples F to J are Comparative Samples. The results of evaluation based on the observation of the surface of each sample are listed in the column of workability in Table 1. In Table 1, the samples marked with "o" have a homogeneous coating and may be utilized as structural members having a smooth surface. The samples marked with "x" have a porous and brittle surface and are not suitable for use as the surface layer of a structural member. Therefore, since the latter samples were not able to be employed in wear tests, they were produced, together with Sample SKD1, by melting and were then subjected to the wear tests.

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Table 1

	C	Cr	V	Mo	W	Nb	Ti	Others	Fe	Workability
A	3.5	30	7	-	3	-	1	-	55.5	0
B	2.5	20	5	10	-	-	-	Zr 2.5	60	0
C	8	35	11	3	5	-	-	-	38	0
D	5	42	5	3	5	-	-	-	40	0
E	6	55	5	3	5	1	1	Hf 2	22	0
F	1.5	40	32	-	-	-	-	-	26.5	X
G	2.5	65	5	-	-	-	-	-	27.5	X
H	3	25	5	35	3	-	-	-	29	X
I	3	25	7	3	30	-	-	-	32	X
J	3	30	7	-	-	-	-	20	-	40
SKD1	2	13	-	-	-	-	-	Si 0.2 Mn 0.4	84.4	-

Fig. 1 is a micrograph, in cross section, of Sample A, as a typical example, in accordance with the present invention. Fig. 2 is a scanning electron micrograph (magnification of 4,000) showing the metal structure, in cross section, of a hard coating of Sample A. As can be seen from these micrographs, notwithstanding the fact that the carbon content is high, an extremely fine structure is achieved. In these micrographs, the phase in which particles are finely and uniformly distributed in the form of blackish gray fragments corresponds to a carbide which is an intermetallic compound. The particles of the carbide phase have a widthwise grain size of 3  $\mu\text{m}$  or less, the areal ratio of the particles is about 70% or greater, and the particles are distributed in the martensite matrix phase (a whitish gray portion in the micrograph) in the form of a wave as a whole. In addition, it will be seen that the distance between adjacent particles of the carbide phase is smaller in the direction normal to the longitudinal direction of the wave than in the longitudinal direction of the same. The hardness of a hard layer constituting the coating is 1200 to 1300 Hv.

Further, after Sample SKD1 had been subjected to heat treatment under the same conditions, its microstructure was observed. As compared with the microstructures shown in Figs. 1 and 2 of Sample A of

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the present invention, the carbide in Sample SKD1 was coarse and non-uniformly distributed. The hardness of Sample SKD1 was about 830 Hv.

Fig. 3 is a graph of the results of the wear tests performed on the aforesaid Samples A to J. A mating material to which Samples A to J were brought into sliding contact was a rolled material of SKD1 having a hardness of 840 Hv, and the wear tests were performed under lubrication conditions employing a turbine oil. The load was 10 MPa (100 kgf/cm<sup>2</sup>), and the number of repetitions was 10<sup>3</sup>. Each of the samples had a sprayed layer of 10 mm in width and 50 mm in length, and the material produced by melting had a trapezoidal shape in cross section with a predetermined thickness. The mating material had a diameter of 8 mm and each of the samples was slid over a distance of 40 mm on the mating material. It will be readily understood from Fig. 3 that Samples A to E of the present invention hardly wear and excel in wear resistance. The wear loss of each of the samples of the present invention was about 0.006 mg/cm<sup>2</sup> or less.

**Example 2**

Samples in Example 2 were prepared in the following manner. An alloy steel (a hard material) having the composition (wt. %) shown in Table 2 was melted, and from the melt a powder having a grain size of 10 to 44 µm was prepared by a vacuum atomizing method. In the same manner as in Example 1, the thus-prepared powder was plasma-sprayed in a reduced pressure atmosphere to a thickness of about 30 µm onto the surface of a base material which was S45C carbon steel specified in the Japanese Industrial Standards. Subsequently, the thus-treated material was carburized in a plasma atmosphere. The carburizing conditions were 1000°C and 20 minutes, and CH<sub>4</sub> was employed as a carburizing gas.

**Table 2**

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	C	Cr	V	Mo	W	Nb	Ti	Hf or Zr	Workability
	K	32	7	-	3	-	1	-	o
	L	2.5	25	5	10	-	-	-	2.5
	M	5	23	11	3	5	-	-	o
	O	5	30	32	-	-	-	-	x
	P	3.5	25	5	3	5	1	1	2
	Q	2.5	50	5	-	-	-	-	x
	H	3	25	5	35	3	-	-	x
	I	3	25	7	3	30	-	-	x
	J	3	30	7	-	-	-	20	-
									x

Samples O, H, I and J are comparative.

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The results of evaluation based on the observation of the surface of each sample are listed in the column of workability in Table 2. In Table 2, the samples marked with "o" have a homogeneous coating and are applicable as a structural member having a smooth surface. In Table 2, Samples O, Q, H, I, and J marked with "x" have a porous and brittle surface and are not suitable for use as the surface layer of a structural member. Therefore, same as in Example 1, materials of these samples were produced by melting. As a typical example, the metal structure, in cross section, of Sample K was observed through a microscope. In consequence, notwithstanding the fact that the content of carbon was high, the structure of the resultant carbide was extremely fine. The particle size of the carbide was finer than that of the as-

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sprayed powder, and the hardness of the surface of the coating was 1200 to 1300 Hv while the hardness of the portion of the coating near the boundary of the base material was 850 Hv. Carburizing was effected over whole of the sprayed layer and the base material. In consequence, the base material was also strengthened. By way of reference, a high carbon-high chromium steel SKD1 (2% C - 13% Cr) produced by a conventional melting method was employed as a comparative material and was carbonitrided. The structure of this material was likewise observed through a microscope. In consequence, the carbonitrides in the structure were coarse and non-uniform as compared with the structure of the material according to the present invention. Further, the hardness of SKD1 was about 830 Hv, and no substantial effect of carbonitriding was obtained.

10 Fig. 4 is a graph of the results of the wear tests. A mating material to which each sample was brought into sliding contact was the same rolled material having a hardness of 840 Hv as in Example 1, and each of the samples was subjected to wear tests under lubrication conditions employing a turbine oil. Each testing condition was the same as in Example 1. As clearly shown in Fig. 4, the wear loss of each of the comparative samples is large, whereas the wear loss of each of the samples of the material of the present invention is about 0.03 mg or less and no substantial wear takes place. Therefore, it will be understood that the samples of the material of the present invention in Example 2 show the wear loss of a degree similar to that in Example 1 and can have excellent wear resistance. Since the materials of the present invention in Example 2 contained a fine carbide, they exhibited a homogeneous wear loss as a whole and no excessive local wear was observed.

15 20 Also, after plasma spraying, the surface layer was subjected to plastic working and was subjected to the same treatment as described above. In consequence, the wear resistance of the surface layer did not change. However, it was found from the observation of the micro-structure that the pores which had been present when no plastic working was effected substantially disappeared, so that the plastic working was very effective in improving the toughness.

25 25 Next, the same samples were subjected to nitriding heat treatment at 550 °C for 5 hours. The hardness of each of the thus-treated samples was 1300 to 1500 Hv, and was higher than the hardness of a carbonitrided one. The wear losses of these samples were the same as those shown in Fig. 4, and the resultant wear resistance was significantly high.

## 30 Example 3

Fig. 5 shows in section an essential portion of a valve lifter for a valve for use in an internal combustion engine. A cylindrical valve lifter 1 for a valve is inserted into a valve-lifter guide bore 3 which is formed in a portion of a cylinder head 2. A valve stem 4 is retained by a valve guide 5 in the center of the guide bore 3 and extends through the cylinder head 2. A coiled valve spring 7 is disposed between the bottom of the guide bore 3 and a retainer 6 fixed to one end of the valve stem 4 by a cotter 5. The spring 7 normally urges the valve stem 4 to move in the direction of a cam shaft 9 to maintain the valve 8 in a closed state. A cam 10 fixed to the cam shaft 9 is pressed into contact with the center of a head 11 of the valve lifter 1. A diffused layer 11a having a thickness of 0.1 mm or greater is formed over the top of the head 11.

35 40 A base body of the valve lifter having a shape shown in Fig. 5 was prepared by cold forging, employing a material called SCM 415. After the surfaces of the base body had been subjected to grid blasting, a hard coating was formed on each of the surfaces by plasma spraying and the durability of the surfaces were compared. One of the plasma spraying processes was spraying in the atmosphere while the other was spraying in a reduced pressure atmosphere. The latter spraying was effected by making a special spraying chamber, reducing the inner pressure of the chamber to 0.1 Torr or less by evacuation, supplying argon gas to the chamber, and maintaining the inner pressure at 6.5 kPa (50 Torr). Plasma for spraying was formed by argon and oxygen gases. The current was about 600 A. The powders to be sprayed has a particle size of 10 to 44 µm and their compositions were: (1) 5% carbon - 25% chromium - 5% vanadium steel; (2) 4.2% carbon - 20% chromium - 3% vanadium - 2% tungsten steel; (3) 5% carbon - 20% chromium - 2% vanadium - 1% niobium steel; (4) 3.5% carbon - 30% chromium - 3% vanadium - 0.5% molybdenum - 0.5% niobium steel; and (5) 3% carbon - 22% chromium - 3% vanadium steel. Each of these powders was produced by a vacuum atomizing method, and was plasma-sprayed to a thickness of 0.5 mm onto the head of the valve lifter as shown in Fig. 5. Some of the valve lifters were compared for durability in their as-sprayed state. Subsequently, the sprayed valve lifters were subjected to the following heat treatment: (1) high-temperature carburizing at 1,000 °C for 15 minutes followed by quenching, similarly to Example 2 or (2) vacuum heat treatment at 1,000 °C for 15 minutes. The oxygen content in the resultant coating changed depending on the spraying method and the heat treatment. More specifically, in each of the coatings obtained by the conventional spraying in the atmosphere, the oxygen content was 5,000 ppm

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or greater, and although there was a tendency that the oxygen content is somewhat reduced by a subsequent heat treatment no significant reduction was observed. Next, in each of the coatings obtained by spraying in the reduced pressure atmosphere, the oxygen content was 1,000 to 4,000 ppm in its as-sprayed state, but it was reduced to 1,000 ppm or less after subjected to the carburizing followed by quenching and to 1,500 ppm or less after subjected to the vacuum heat treatment. The hardness of the surface in each of the coatings obtained by spraying in the atmosphere was 400 to 750 Hv in its as-sprayed state and thus its dispersion was large. This dispersion was not made homogeneous by the heat treatment. Next, the hardness of the surface in each of the coatings obtained by spraying in the reduced pressure atmosphere was 500 to 970 Hv in its as-sprayed state and thus its dispersion was large. However, when it was subsequently subjected to the carburizing followed by quenching, the hardness became 800 to 1,000 Hv and thus the dispersion in hardness became small.

Fig. 6 shows a microstructure at the boundary between the coating and the base material. Fig. 7 is a graph showing the distribution of the hardness in the material having a sprayed coating subjected to carburizing followed by quenching of the aforesaid (1). A larger number of oxide pores were present in the coating obtained by spraying in the atmosphere in comparison with the coating obtained by spraying in the reduced pressure atmosphere. The oxide pores were hardly changed by a subsequent heat treatment, and constituted a cause of embrittlement. The durabilities of the respective products having the sprayed coating were compared with one another, and it was found that the one carburized after spraying in the reduced pressure atmosphere exhibited the maximum durability. The product having the coating obtained by spraying in the atmosphere exhibited in wear tests a pitting phenomenon in the as-sprayed state and in the heat-treated state in short period of time, and its durability was about 1/3 of the aforesaid maximum durability. The durability of the product having the coating obtained by spraying in the reduced pressure atmosphere in the as-sprayed state was about 1/2 to 4/5 of that of the product carburized after spraying. In some of the products the coating exfoliated from the base material during long-time repetition of wear tests. The durability of the product having the coating obtained by spraying in the reduced pressure atmosphere and subjected to the vacuum heat treatment was 3/4 to 1.0 of that of the product having the coating obtained by spraying in the reduced pressure atmosphere and subjected to the carburizing. The former product worn in its surface but no exfoliation of the coating was observed. When a cross section of this product was observed through a microscope, a diffused layer was formed between the base material and the coating. In case of the product having the coating obtained by spraying in the atmosphere, such a diffused layer was not clearly observed when it was subsequently heat-treated.

Although the hard coating 11a is formed by spraying over the head 11 of the valve lifter 1, the hard coating 11a may additionally be formed over a sliding portion 10a of the cam 10 subjected to the highest pressure as shown in Fig. 5 or over the entire circumference of the cam 10. Of course, such a hard coating may be formed as required over both or either of the sliding surfaces.

Fig. 8 shows another embodiment. As illustrated, a hard coating 20a is formed over a surface 20b of a rocker arm 20 in contact with one end of the valve stem 4 as well as a rear surface 20c in contact with the circumference of the cam 10. The hard coatings 20a and the hard coating 11a over the sliding portion 10a of the cam 10 cooperate with one another in improving the wear resistance of the sliding portions of the valve mechanism.

Fig. 9 shows still another embodiment, wherein one end of the valve stem 4 is fixed to one end of a rocker arm 21, and a hard coating 21a is formed over a sliding portion 21b of the rocker arm 21 while the hard coating 11a is formed over the sliding portion 10a of the cam 10. These coatings may be formed as required over both or either of the surfaces which are brought into sliding contact with each other.

45

**Claims**

1. A wear-resistant metal member having a surface which has a sprayed layer which consists essentially of, by weight,
  - 50 2 to 10% C,
  - 18 to 60% Cr,
  - 0.3 to 20% V,
  - optionally 25% or less Mo,
  - optionally 25% or less W,
  - 55 optionally 15% or less Nb,
  - optionally 10% or less Ti,
  - optionally 10% or less Zr,
  - optionally 10% or less Hf,

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optionally 15% or less Ta,  
 optionally 2% or less Si,  
 optionally 2% or less Mn,  
 optionally, boron incorporated by diffusion  
 5 into the surface of the layer,  
 balance Fe in an amount of 20% or more,  
 said sprayed layer having an oxygen concentration less than 1500 ppm and a martensite-phase matrix containing carbide particles, nitride particles or carbonitride particles, said particles having a size of 3  $\mu\text{m}$  or less and an areal ratio in the range 25 to 90%.  
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2. A wear-resistant metal member according to claim 1 wherein said particles are formed mainly in such a state that numerous of said particles are bonded together.  
 15

3. A wear-resistant metal member according to claim 1 or claim 2 in which said sprayed layer has been subjected to tempering, after the quench-hardening.  
 20

4. A wear-resistant metal member according to any one of claims 1 to 3 wherein said layer has a surface region which is carburized, nitrided, carbonitrided, or subjected to diffusion of boron to form boride.  
 25

5. A wear-resistant metal member according to any one of the preceding claims wherein said layer consists essentially of, by weight,  
 2.5 to 5% C,  
 25 to 35% Cr,  
 3 to 11% V,  
 30 optionally 25% or less Mo,  
 optionally 25% or less W,  
 optionally 15% or less Nb,  
 optionally 10% or less Ti,  
 optionally 10% or less Zr,  
 optionally 10% or less Hf,  
 the balance being substantially Fe.  
 35

6. A method of producing a wear-resistant metal member, comprising the steps of:  
 spraying an alloy onto a surface of a metal member under reduced pressure in a non-oxidizing atmosphere by plasma spraying to form a sprayed layer on said surface, and thereafter  
 either (i) subjecting said sprayed layer to a hardening treatment consisting of heating at a predetermined temperature followed by quenching, and optionally, subjecting said sprayed layer to a tempering treatment, or (ii) subjecting said sprayed layer to a vacuum heat treatment to reduce its oxygen content;  
 40

the components of said alloy being selected to provide, after said treatment, said layer having a composition by weight essentially of:  
 2 to 10% C,  
 18 to 60% Cr,  
 0.3 to 20% V,  
 45 less than 1500 ppm oxygen,  
 optionally 25% or less Mo,  
 optionally 25% or less W,  
 optionally 15% or less Nb,  
 optionally 10% or less Ti,  
 50 optionally 10% or less Zr,  
 optionally 10% or less Hf,  
 optionally 15% or less Ta,  
 optionally 2% or less Si,  
 optionally 2% or less Mn,  
 55 optionally, boron incorporated by diffusion into the surface of the layer,  
 balance Fe in an amount of 20% or more,

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7. A method according to claim 6 including, after spraying of the alloy, carburizing, nitriding, carbonitriding or bording of said sprayed layer.

8. A method according to claim 6 wherein the hardening and quenching treatment is included and comprises:  
5 subjecting said sprayed layer to a carburizing nitriding or carbonitriding treatment; quench-hardening said sprayed layer from a predetermined temperature; and then tempering said sprayed layer by heating it at a predetermined temperature.

10. 9. A method according to any one of claims 6 to 8 including, before said hardening, subjecting said sprayed layer to a hot plastic working.

15. 10. A wear-resistant sliding mechanism comprising metal members which are maintained in sliding contact with each other, at least one of said metal members being as claimed in any one of claims 1 to 5 or produced by a method according to any one of claims 6 to 9.

20. 11. A valve gear for use in an internal combustion engine which is adapted to employ a thrust generated by the rotation of a cam to cause a valve stem to reciprocally move, said valve gear comprising metal members which are maintained in sliding contact with each other, at least one of said metal members being a metal member having a sprayed layer as claimed in any one of claims 1 to 5 or produced by a method according to any one of claims 6 to 9.

25. 12. The valve gear according to claim 11 wherein said sprayed layer is a hard coating having a thickness of 0.1 to 0.75 mm.

13. The valve gear according to claim 11 or claim 12 wherein the oxygen content in said sprayed layer is 1500 ppm or less.

30. 14. The valve gear according to claim 11, claim 12 or claim 13 wherein said metal member having said sprayed layer is a valve lifter, wherein the carbon content in said valve lifter is 0.1 to 0.4%.

35. 15. The valve gear according to any one of claims 11 to 13 wherein said metal member having a sprayed layer contacts a cam wheel and the carbon concentration in the surface of said sprayed layer which comes into sliding contact with the cam wheel is higher than that in the portion of said sprayed layer adjacent to a base material of said metal member.

16. A valve gear according to any one of claims 11 to 15 wherein said sprayed layer is on a valve lifter and the sprayed layer and the body of the valve lifter are bonded together by a diffused layer.

**40 Patentansprüche**

1. Verschleißbeständiges Metallteil mit einer Oberfläche mit einer gesprühten Schicht, die gewichtsbezogen hauptsächlich aus folgendem besteht:  
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- 2 bis 10 % C,
- 18 bis 60 % Cr,
- 0,3 bis 20 % V,
- wahlweise 25 % oder weniger Mo,
- wahlweise 25 % oder weniger W,
- wahlweise 15 % oder weniger Nb,

50

- wahlweise 10 % oder weniger Ti,
- wahlweise 10 % oder weniger Zr,
- wahlweise 10 % oder weniger Hf,
- wahlweise 15 % oder weniger Ta,
- wahlweise 2 % oder weniger Si,

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- wahlweise 2 % oder weniger Mn,
- wahlweise Bor, das durch Diffusion in die Oberfläche der Schicht eingebaut ist,
- Eisen als Rest mit einer Menge von 20 % oder mehr,

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- wobei die gesprührte Schicht eine Sauerstoffkonzentration unter 1500 ppm und eine Carbidteilchen, Nitridteilchen oder Carbonitridteilchen enthaltende Matrix in der Martensitphase aufweist, wobei die Teilchen eine Größe von 3 µm oder weniger und ein Flächenverhältnis im Bereich von 25 bis 90 % aufweisen.

5           **2.** Verschleißbeständiges Metallteil nach Anspruch 1, bei dem die Teilchen hauptsächlich in einem solchen Zustand ausgebildet sind, daß zahlreiche Teilchen aneinander haften.

10          **3.** Verschleißbeständiges Metallteil nach Anspruch 1 oder Anspruch 2, bei dem die aufgesprührte Schicht nach einem Abschreckhärten einem Temperiern unterzogen wurde.

15          **4.** Verschleißbeständiges Metallteil nach einem der Ansprüche 1 bis 3, bei dem die Schicht einen Oberflächenbereich aufweist, der carbiert, nitriert, carbonitiert oder einer Diffusion von Bor zum Bilden von Borid unterzogen ist.

20          **5.** Verschleißbeständiges Metallteil nach einem der vorstehenden Ansprüche, bei dem die Schicht gewichtsbezogen hauptsächlich aus folgendem besteht:
 

- 2,5 bis 5 % C,
- 25 bis 35 % Cr,
- 3 bis 11 % V,
- wahlweise 25 % oder weniger Mo,
- wahlweise 25 % oder weniger W,
- wahlweise 15 % oder weniger Nb,
- wahlweise 10 % oder weniger Ti,
- wahlweise 10 % oder weniger Zr,
- wahlweise 10 % oder weniger Hf,
- wobei der Rest im wesentlichen Fe ist.

25          **6.** Verfahren zum Herstellen eines verschleißbeständigen Metallteils, mit den folgenden Schritten:
 

- Aufsprühen einer Legierung auf eine Oberfläche eines Metallteils unter verringertem Druck in nichtoxidierender Atmosphäre durch einen Plasmaaufsprühvorgang zum Ausbilden einer aufgesprührten Schicht auf der Fläche, und anschließend
- entweder (i) Unterziehen der aufgesprührten Schicht einer Härtungsbehandlung, die aus einem Erhitzen auf eine vorgegebene Temperatur gefolgt von einem Abschrecken und, wahlweise, darin besteht, daß die aufgesprührte Schicht einer Temperbehandlung unterzogen wird, oder (ii) Unterziehen der aufgesprührten Schicht einer Wärmebehandlung im Vakuum zum Verringern des Sauerstoffgehalts derselben;
- wobei die Komponenten der Legierung so ausgewählt sind, daß sich nach der Behandlung eine Schicht mit einer gewichtsbezogenen Zusammensetzung im wesentlichen aus dem folgenden ergibt:
  - 2 bis 10 % C,
  - 18 bis 60 % Cr,
  - 0,3 bis 20 % V,
  - unter 1500 ppm Sauerstoff,
  - wahlweise 25 % oder weniger Mo,
  - wahlweise 25 % oder weniger W,
  - wahlweise 15 % oder weniger Nb,
  - wahlweise 10 % oder weniger Ti,
  - wahlweise 10 % oder weniger Zr,
  - wahlweise 10 % oder weniger Hf,
  - wahlweise 15 % oder weniger Ta,
  - wahlweise 2 % oder weniger Si,
  - wahlweise 2 % oder weniger Mn,
  - wahlweise Bor, das durch Diffusion in die Oberfläche der Schicht eingebaut ist,
  - Eisen als Rest mit einer Menge von 20 % oder mehr.

30          **7.** Verfahren nach Anspruch 6 mit einem Carburieren, Nitrieren, Carbonitrieren oder Borieren der aufgesprührten Schicht nach dem Aufsprühen der Legierung.

35          **8.** Verfahren zum Herstellen eines verschleißbeständigen Metallteils, mit den folgenden Schritten:
 

- Aufsprühen einer Legierung auf eine Oberfläche eines Metallteils unter verringertem Druck in nichtoxidierender Atmosphäre durch einen Plasmaaufsprühvorgang zum Ausbilden einer aufgesprührten Schicht auf der Fläche, und anschließend
- entweder (i) Unterziehen der aufgesprührten Schicht einer Härtungsbehandlung, die aus einem Erhitzen auf eine vorgegebene Temperatur gefolgt von einem Abschrecken und, wahlweise, darin besteht, daß die aufgesprührte Schicht einer Temperbehandlung unterzogen wird, oder (ii) Unterziehen der aufgesprührten Schicht einer Wärmebehandlung im Vakuum zum Verringern des Sauerstoffgehalts derselben;
- wobei die Komponenten der Legierung so ausgewählt sind, daß sich nach der Behandlung eine Schicht mit einer gewichtsbezogenen Zusammensetzung im wesentlichen aus dem folgenden ergibt:
  - 2 bis 10 % C,
  - 18 bis 60 % Cr,
  - 0,3 bis 20 % V,
  - unter 1500 ppm Sauerstoff,
  - wahlweise 25 % oder weniger Mo,
  - wahlweise 25 % oder weniger W,
  - wahlweise 15 % oder weniger Nb,
  - wahlweise 10 % oder weniger Ti,
  - wahlweise 10 % oder weniger Zr,
  - wahlweise 10 % oder weniger Hf,
  - wahlweise 15 % oder weniger Ta,
  - wahlweise 2 % oder weniger Si,
  - wahlweise 2 % oder weniger Mn,
  - wahlweise Bor, das durch Diffusion in die Oberfläche der Schicht eingebaut ist,
  - Eisen als Rest mit einer Menge von 20 % oder mehr.

40          **9.** Verfahren zum Herstellen eines verschleißbeständigen Metallteils, mit den folgenden Schritten:
 

- Aufsprühen einer Legierung auf eine Oberfläche eines Metallteils unter verringertem Druck in nichtoxidierender Atmosphäre durch einen Plasmaaufsprühvorgang zum Ausbilden einer aufgesprührten Schicht auf der Fläche, und anschließend
- entweder (i) Unterziehen der aufgesprührten Schicht einer Härtungsbehandlung, die aus einem Erhitzen auf eine vorgegebene Temperatur gefolgt von einem Abschrecken und, wahlweise, darin besteht, daß die aufgesprührte Schicht einer Temperbehandlung unterzogen wird, oder (ii) Unterziehen der aufgesprührten Schicht einer Wärmebehandlung im Vakuum zum Verringern des Sauerstoffgehalts derselben;
- wobei die Komponenten der Legierung so ausgewählt sind, daß sich nach der Behandlung eine Schicht mit einer gewichtsbezogenen Zusammensetzung im wesentlichen aus dem folgenden ergibt:
  - 2 bis 10 % C,
  - 18 bis 60 % Cr,
  - 0,3 bis 20 % V,
  - unter 1500 ppm Sauerstoff,
  - wahlweise 25 % oder weniger Mo,
  - wahlweise 25 % oder weniger W,
  - wahlweise 15 % oder weniger Nb,
  - wahlweise 10 % oder weniger Ti,
  - wahlweise 10 % oder weniger Zr,
  - wahlweise 10 % oder weniger Hf,
  - wahlweise 15 % oder weniger Ta,
  - wahlweise 2 % oder weniger Si,
  - wahlweise 2 % oder weniger Mn,
  - wahlweise Bor, das durch Diffusion in die Oberfläche der Schicht eingebaut ist,
  - Eisen als Rest mit einer Menge von 20 % oder mehr.

45          **10.** Verfahren zum Herstellen eines verschleißbeständigen Metallteils, mit den folgenden Schritten:
 

- Aufsprühen einer Legierung auf eine Oberfläche eines Metallteils unter verringertem Druck in nichtoxidierender Atmosphäre durch einen Plasmaaufsprühvorgang zum Ausbilden einer aufgesprührten Schicht auf der Fläche, und anschließend
- entweder (i) Unterziehen der aufgesprührten Schicht einer Härtungsbehandlung, die aus einem Erhitzen auf eine vorgegebene Temperatur gefolgt von einem Abschrecken und, wahlweise, darin besteht, daß die aufgesprührte Schicht einer Temperbehandlung unterzogen wird, oder (ii) Unterziehen der aufgesprührten Schicht einer Wärmebehandlung im Vakuum zum Verringern des Sauerstoffgehalts derselben;
- wobei die Komponenten der Legierung so ausgewählt sind, daß sich nach der Behandlung eine Schicht mit einer gewichtsbezogenen Zusammensetzung im wesentlichen aus dem folgenden ergibt:
  - 2 bis 10 % C,
  - 18 bis 60 % Cr,
  - 0,3 bis 20 % V,
  - unter 1500 ppm Sauerstoff,
  - wahlweise 25 % oder weniger Mo,
  - wahlweise 25 % oder weniger W,
  - wahlweise 15 % oder weniger Nb,
  - wahlweise 10 % oder weniger Ti,
  - wahlweise 10 % oder weniger Zr,
  - wahlweise 10 % oder weniger Hf,
  - wahlweise 15 % oder weniger Ta,
  - wahlweise 2 % oder weniger Si,
  - wahlweise 2 % oder weniger Mn,
  - wahlweise Bor, das durch Diffusion in die Oberfläche der Schicht eingebaut ist,
  - Eisen als Rest mit einer Menge von 20 % oder mehr.

50          **11.** Verfahren zum Herstellen eines verschleißbeständigen Metallteils, mit den folgenden Schritten:
 

- Aufsprühen einer Legierung auf eine Oberfläche eines Metallteils unter verringertem Druck in nichtoxidierender Atmosphäre durch einen Plasmaaufsprühvorgang zum Ausbilden einer aufgesprührten Schicht auf der Fläche, und anschließend
- entweder (i) Unterziehen der aufgesprührten Schicht einer Härtungsbehandlung, die aus einem Erhitzen auf eine vorgegebene Temperatur gefolgt von einem Abschrecken und, wahlweise, darin besteht, daß die aufgesprührte Schicht einer Temperbehandlung unterzogen wird, oder (ii) Unterziehen der aufgesprührten Schicht einer Wärmebehandlung im Vakuum zum Verringern des Sauerstoffgehalts derselben;
- wobei die Komponenten der Legierung so ausgewählt sind, daß sich nach der Behandlung eine Schicht mit einer gewichtsbezogenen Zusammensetzung im wesentlichen aus dem folgenden ergibt:
  - 2 bis 10 % C,
  - 18 bis 60 % Cr,
  - 0,3 bis 20 % V,
  - unter 1500 ppm Sauerstoff,
  - wahlweise 25 % oder weniger Mo,
  - wahlweise 25 % oder weniger W,
  - wahlweise 15 % oder weniger Nb,
  - wahlweise 10 % oder weniger Ti,
  - wahlweise 10 % oder weniger Zr,
  - wahlweise 10 % oder weniger Hf,
  - wahlweise 15 % oder weniger Ta,
  - wahlweise 2 % oder weniger Si,
  - wahlweise 2 % oder weniger Mn,
  - wahlweise Bor, das durch Diffusion in die Oberfläche der Schicht eingebaut ist,
  - Eisen als Rest mit einer Menge von 20 % oder mehr.

55          **12.** Verfahren zum Herstellen eines verschleißbeständigen Metallteils, mit den folgenden Schritten:
 

- Aufsprühen einer Legierung auf eine Oberfläche eines Metallteils unter verringertem Druck in nichtoxidierender Atmosphäre durch einen Plasmaaufsprühvorgang zum Ausbilden einer aufgesprührten Schicht auf der Fläche, und anschließend
- entweder (i) Unterziehen der aufgesprührten Schicht einer Härtungsbehandlung, die aus einem Erhitzen auf eine vorgegebene Temperatur gefolgt von einem Abschrecken und, wahlweise, darin besteht, daß die aufgesprührte Schicht einer Temperbehandlung unterzogen wird, oder (ii) Unterziehen der aufgesprührten Schicht einer Wärmebehandlung im Vakuum zum Verringern des Sauerstoffgehalts derselben;
- wobei die Komponenten der Legierung so ausgewählt sind, daß sich nach der Behandlung eine Schicht mit einer gewichtsbezogenen Zusammensetzung im wesentlichen aus dem folgenden ergibt:
  - 2 bis 10 % C,
  - 18 bis 60 % Cr,
  - 0,3 bis 20 % V,
  - unter 1500 ppm Sauerstoff,
  - wahlweise 25 % oder weniger Mo,
  - wahlweise 25 % oder weniger W,
  - wahlweise 15 % oder weniger Nb,
  - wahlweise 10 % oder weniger Ti,
  - wahlweise 10 % oder weniger Zr,
  - wahlweise 10 % oder weniger Hf,
  - wahlweise 15 % oder weniger Ta,
  - wahlweise 2 % oder weniger Si,
  - wahlweise 2 % oder weniger Mn,
  - wahlweise Bor, das durch Diffusion in die Oberfläche der Schicht eingebaut ist,
  - Eisen als Rest mit einer Menge von 20 % oder mehr.

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8. Verfahren nach Anspruch 6, bei dem die Härtungs- und Abschreckbehandlung vorgenommen wird und folgendes aufweist:

- Unterziehen der aufgesprühten Schicht einer carburierenden, nitrierenden oder carbonitrierenden Behandlung;
- Abschreckhärteln der aufgesprühten Schicht ausgehend von einer vorgegebenen Temperatur; und dann
- Temperiern der aufgesprühten Schicht durch Aufheizen derselben auf eine vorgegebene Temperatur.

10 9. Verfahren nach einem der Ansprüche 6 bis 8, bei dem die aufgesprühte Schicht vor dem Härteln einer plastischen Heißverformung unterzogen wird.

10 10. Verschleißbeständiger Gleitmechanismus mit Metallteilen, die in Gleitkontakt miteinander gehalten werden, wobei mindestens eines der Metallteile ein solches ist, wie in einem der Ansprüche 1 bis 5 beansprucht oder wie es durch ein Verfahren gemäß einem der Ansprüche 6 bis 9 hergestellt wurde.

20 11. Ventiltrieb zur Verwendung in einem Verbrennungsmotor, der so ausgebildet ist, daß er eine von der Umdrehung eines Nockens erzeugte Schubkraft dazu verwendet, einen Ventilschaft hin und her zu bewegen, wobei der Ventiltrieb Metallteile aufweist, die in Gleitkontakt miteinander gehalten werden, wobei mindestens eines der Metallteile ein solches ist, das eine aufgesprühte Schicht aufweist, wie in einem der Ansprüche 1 bis 5 beansprucht oder wie durch ein Verfahren gemäß einem der Ansprüche 6 bis 9 hergestellt.

25 12. Ventiltrieb nach Anspruch 11, bei dem die aufgesprühte Schicht eine harte Beschichtung mit einer Dicke von 0,1 bis 0,75 mm ist.

13. Ventiltrieb nach Anspruch 11 oder Anspruch 12, bei dem der Sauerstoffgehalt in der gesprühten Schicht 1500 ppm oder weniger beträgt.

30 14. Ventiltrieb nach Anspruch 11, Anspruch 12 oder Anspruch 13, bei dem das Metallteil mit der aufgesprühten Schicht ein Ventilstößel ist, wobei der Kohlenstoffgehalt im Ventilstößel 0,1 bis 0,4 % beträgt.

35 15. Ventiltrieb nach einem der Ansprüche 11 bis 13, bei dem das Metallteil mit der aufgesprühten Schicht ein Nockenrad kontaktiert und die Kohlenstoffkonzentration in der Oberfläche der aufgesprühten Schicht, die in Gleitkontakt mit dem Nockenrad kommt, höher ist als im Teil der gesprühten Schicht, die an das Trägermaterial des Metallteils angrenzt.

40 16. Ventiltrieb nach einem der Ansprüche 11 bis 15, bei dem die aufgesprühte Schicht auf einem Ventilstößel vorliegt und die aufgesprühte Schicht und der Körper des Ventilstößels über eine Diffusionsschicht miteinander verbunden sind.

## Revendications

45 1. Un élément en métal résistant à l'usure, ayant une surface qui a une couche déposée par projection, qui se compose essentiellement en poids de :

- 2 à 10% de C,
- 18 à 60% de Cr,
- 0,3 à 20% de V,

50 facultativement de 25% ou moins de Mo,

facultativement de 25% ou moins de W,

facultativement de 15% ou moins de Nb,

facultativement de 10% ou moins de Ti,

facultativement de 10% ou moins de Zr,

55 facultativement de 10% ou moins de Hf,

facultativement de 15% ou moins de Ta,

facultativement de 2% ou moins de Si,

facultativement de 2% ou moins de Mn,

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facultativement de bore incorporé par diffusion dans la surface de la couche,  
le reste en Fe en une quantité de 20% ou plus,  
ladite couche déposée par projection ayant une concentration en oxygène inférieure à 1500 ppm et une matrice à phase de martensite contenant des particules de carbure, des particules de nitrule ou des particules de carbonitrure, lesdites particules ayant une grosseur de 3 µm ou moins et un rapport d'aire dans le domaine de 25 à 90%.

2. Un élément en métal résistant à l'usure selon la revendication 1, dans lequel lesdites particules sont formées principalement dans un état tel que beaucoup desdites particules sont liées ensemble.

3. Un élément en métal résistant à l'usure selon la revendication 1 ou la revendication 2, dans lequel ladite couche projetée a été soumise à un revenu après le durcissement par refroidissement rapide.

4. Un élément en métal résistant à l'usure selon l'une quelconque des revendications 1 à 3, dans lequel ladite couche a une région de surface qui est carburée, nitrurée, carbonitrurée ou soumise à une diffusion de bore pour former du borure.

5. Un élément en métal résistant à l'usure selon l'une quelconque des revendications précédentes, dans lequel ladite couche se compose essentiellement en poids de :  
2,5 à 5% de C,  
25 à 35% de Cr,  
3 à 11% de V,  
facultativement de 25% ou moins de Mo,  
facultativement de 25% ou moins de W,  
facultativement de 15% ou moins de Nb,  
facultativement de 10% ou moins de Ti,  
facultativement de 10% ou moins de Zr,  
facultativement de 10% ou moins de Hf,  
le reste étant sensiblement du Fe.

6. Un procédé de production d'un élément en métal résistant à l'usure, comprenant les opérations consistant :  
à pulvériser un alliage sur une surface d'un élément en métal sous pression réduite dans une atmosphère non oxydante par projection à plasma pour former une couche déposée par projection sur ladite surface et, ensuite  
soit (i) à soumettre ladite couche déposée par pulvérisation à un traitement de durcissement consistant en un chauffage à une température prédéterminée suivi d'une trempe et, facultativement, à soumettre ladite couche déposée par projection à un traitement de revenu ou (ii) à soumettre ladite couche déposée par pulvérisation à un traitement thermique sous vide pour réduire sa teneur en oxygène; les composants dudit alliage étant choisis pour former, après ledit traitement, ladite couche ayant une composition en poids essentiellement de :  
2 à 10% de C,  
18 à 60% de Cr,  
0,3 à 20% de V,  
moins de 1500 ppm d'oxygène,  
facultativement 25% ou moins de Mo,  
facultativement 25% ou moins de W,  
facultativement 15% ou moins de Nb,  
facultativement 10% ou moins de Ti,  
facultativement 10% ou moins de Zr,  
facultativement 10% ou moins de Hf,  
facultativement 15% ou moins de Ta,  
facultativement 2% ou moins de Si,  
facultativement 2% ou moins de Mn,  
facultativement du bore incorporé par diffusion dans la surface de la couche,  
le reste en Fe en une quantité de 20% ou plus.

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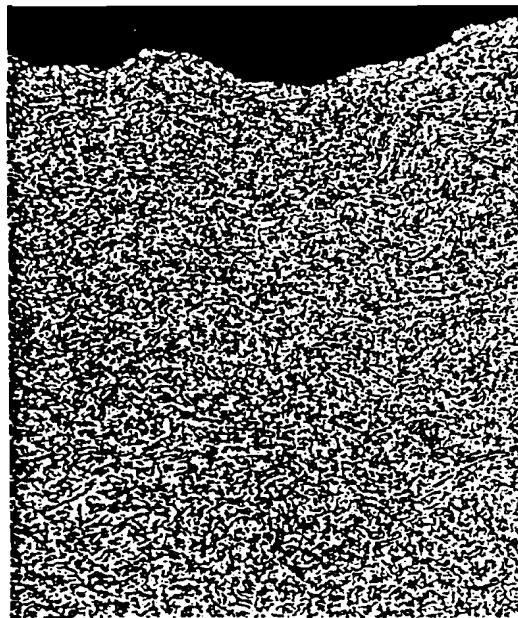
7. Un procédé selon la revendication 6, comprenant, après la projection de l'alliage, la carburation, la nitridation, la carbonitridation ou la boruration de ladite couche déposée par pulvérisation.
8. Un procédé selon la revendication 6, dans lequel le traitement de durcissement et de trempe est inclus et comprend :
  - la soumission de ladite couche déposée par projection à un traitement de carburation, de nitridation ou de carbonitridation;
  - la trempe par refroidissement rapide de ladite couche déposée par pulvérisation depuis une température prédéterminée; et ensuite
  - le revenu de ladite couche déposée par projection en la chauffant à une température prédéterminée.
10. Un procédé selon l'une quelconque des revendications 6 à 8, comprenant, avant ledit durcissement, la soumission de ladite couche déposée par pulvérisation à un façonnage plastique à chaud.
15. 10. Un mécanisme coulissant résistant à l'usure comprenant des organes en métal qui sont maintenus en contact glissant les uns avec les autres, au moins l'un desdits éléments en métal étant tel que revendiqué dans l'une quelconque des revendications 1 à 5 ou produit par un procédé selon l'une quelconque des revendications 6 à 9.
20. 11. Un mécanisme de commande de soupape pour utilisation dans un moteur à combustion interne, qui est adapté pour employer une poussée engendrée par la rotation d'une came pour forcer une tige de soupape à se mouvoir alternativement, ledit mécanisme de commande de soupape comprenant des éléments en métal qui sont maintenus en contact glissant les uns avec les autres, au moins l'un desdits éléments en métal étant un élément en métal ayant une couche déposée par pulvérisation, telle que revendiquée dans l'une quelconque des revendications 1 à 5 ou produite par un procédé selon l'une quelconque des revendications 6 à 9.
25. 12. Le mécanisme de commande de soupape selon la revendication 11, dans lequel ladite couche déposée par projection est un revêtement dur ayant une épaisseur de 0,1 à 0,75 mm.
30. 13. Le mécanisme de commande de soupape selon la revendication 11 ou la revendication 12, dans lequel la teneur en oxygène de ladite couche déposée par pulvérisation est de 1500 ppm ou moins.
35. 14. Le mécanisme de commande de soupape selon la revendication 11, la revendication 12 ou la revendication 13, dans lequel ledit élément en métal ayant ladite couche déposée par pulvérisation est un poussoir de soupape, dans lequel la teneur en carbone dudit poussoir de soupape est de 0,1 à 0,4%.
40. 15. Le mécanisme de commande de soupape selon l'une quelconque des revendications 11 à 13, dans lequel ledit élément en métal, ayant une couche déposée par pulvérisation, est en contact avec une roue formant came et la concentration de carbone dans la surface de ladite couche déposée par projection, qui vient en contact glissant avec la roue formant came, est supérieure à celle dans la partie de ladite couche déposée par projection qui est adjacente à une matière de base dudit élément en métal.
45. 16. Un mécanisme de commande de soupape selon l'une quelconque des revendications 11 à 16, dans lequel ladite couche déposée par pulvérisation est placée sur un poussoir de soupape et ladite couche déposée par pulvérisation et le corps du poussoir de soupape sont liés ensemble par une couche diffusée.

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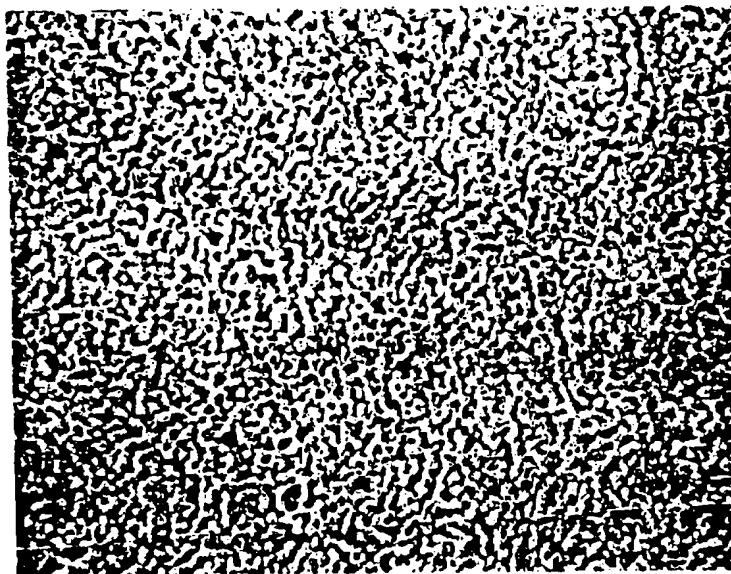
**FIG. I**



$25\mu\text{m}$

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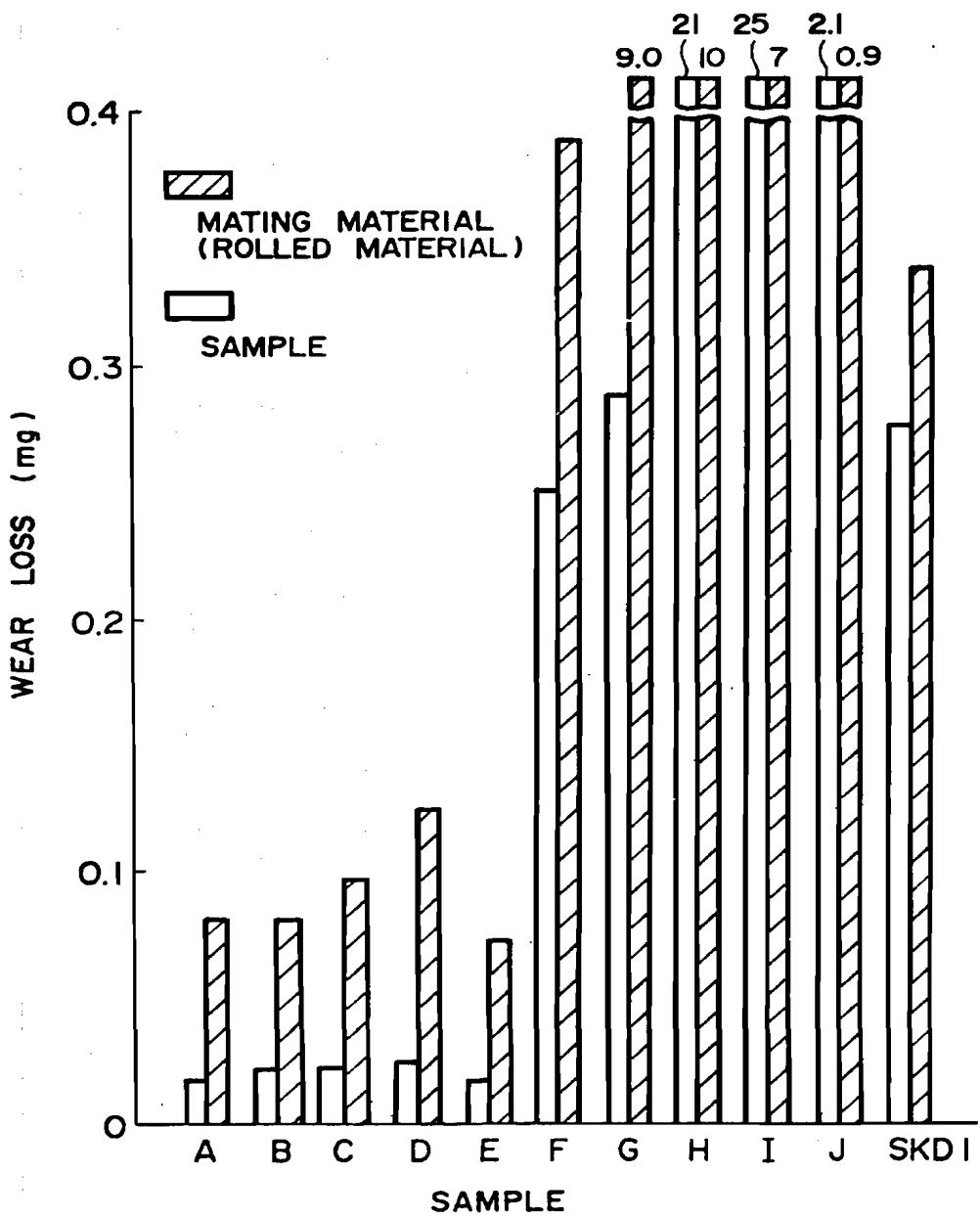
**FIG. 2**



**$5 \mu\text{m}$**

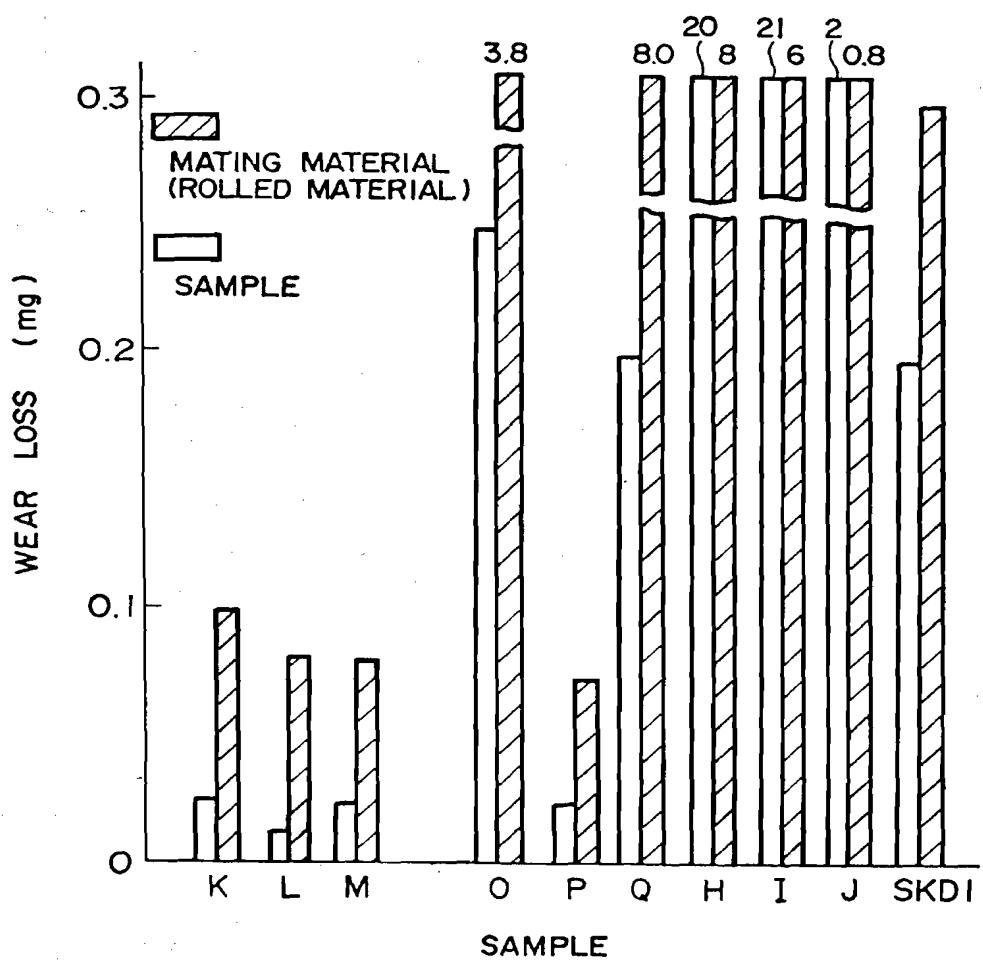
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FIG. 3



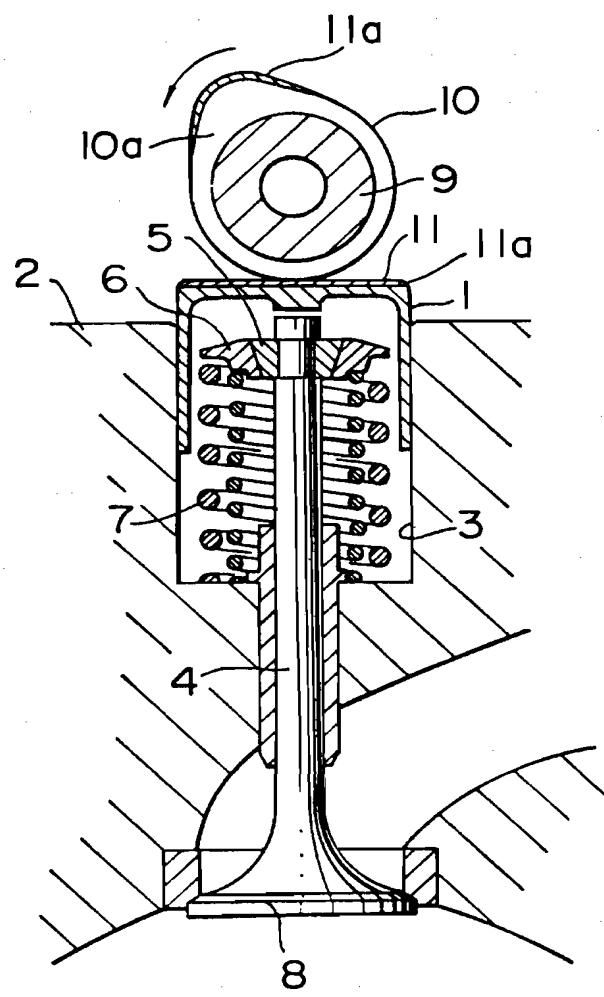
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FIG. 4



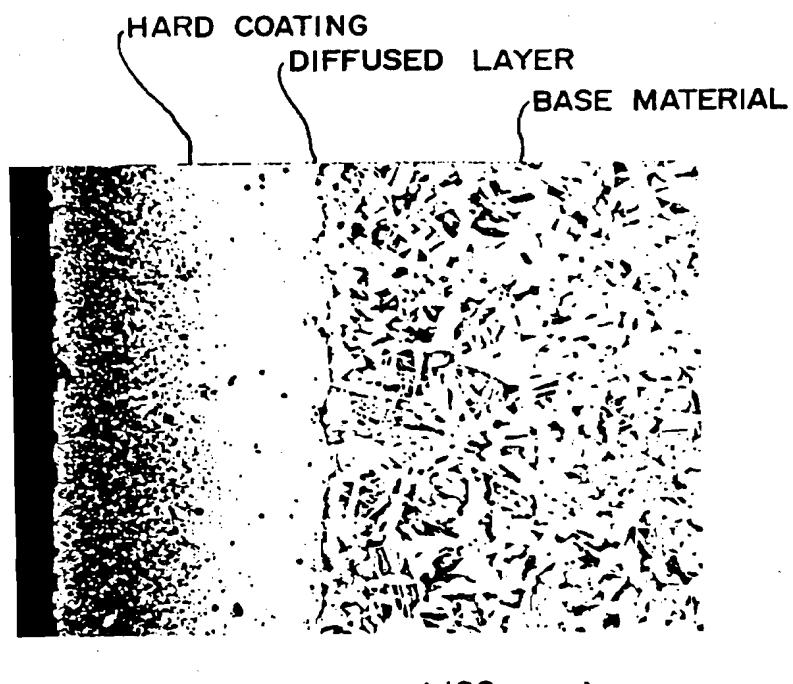
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FIG. 5



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FIG. 6

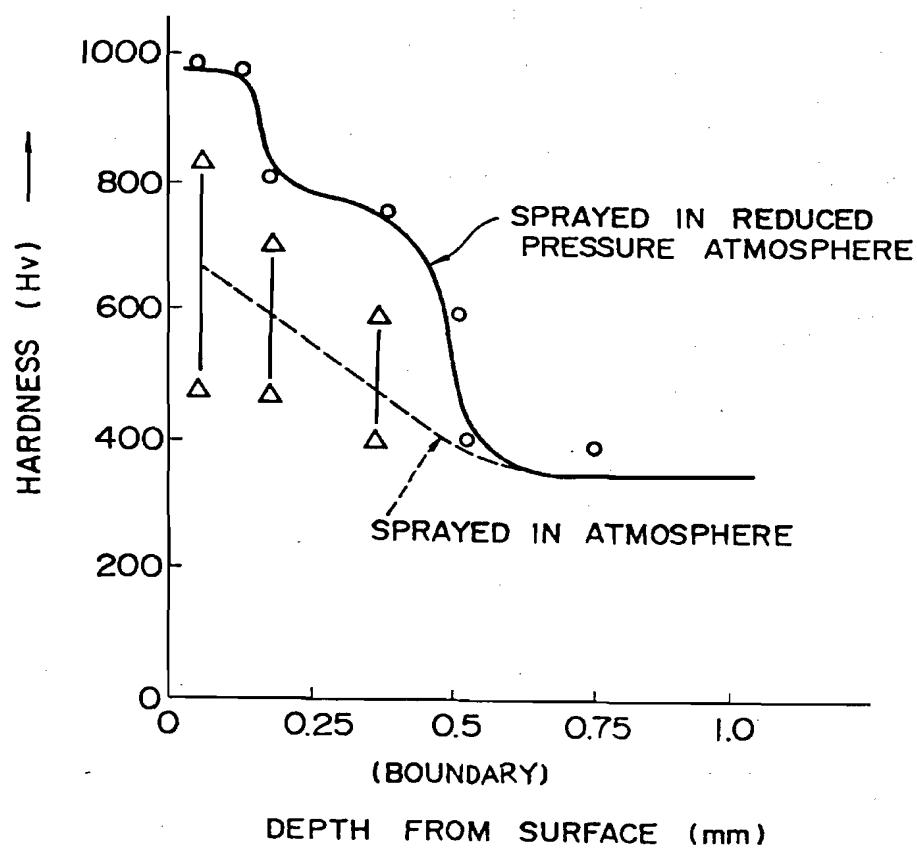


( 100  $\mu\text{m}$  )

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FIG. 7



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FIG. 8

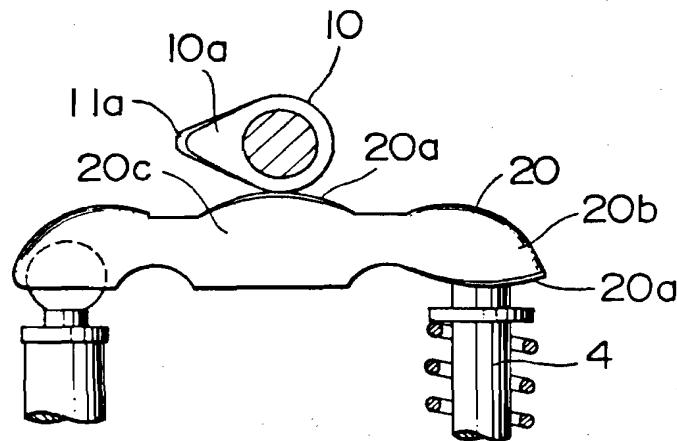
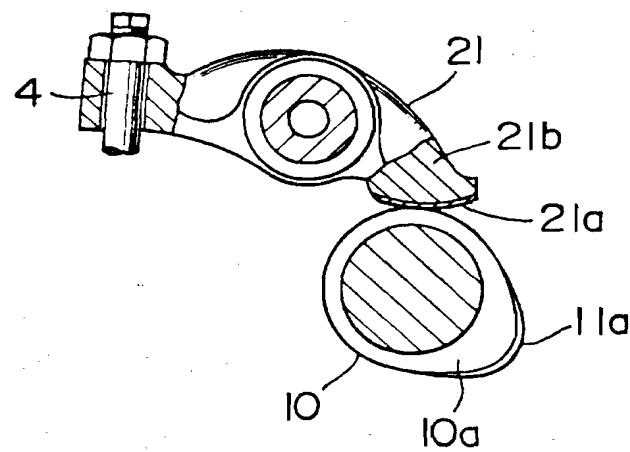


FIG. 9



# INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2005/000191

## A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. 7: C23C 26/02, 30/00, C22C 33/04, 38/18, 38/22, 38/24, 38/28, 38/32, B23K 35/22, 35/24,

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC<sup>7</sup> as above

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
Derwent WPI: IPC<sup>7</sup> as above and (chromium or carbid+ or homog+ or hardfac+)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 266149 B1 (Hitachi Ltd) 4 January 1995 Whole Document	
A	GB 1504577 A (GFE Gesellschaft) 22 March 1978 Whole Document	
A	GB 1504547 A (Sintermetallwerk Krebsoge) 22 March 1978 Whole Document	
A	CA 2149010 A1 (Gleixner et al) 11 October 1995 Whole Document	

Further documents are listed in the continuation of Box C

See patent family annex

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the International filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the International filing date but later than the priority date claimed	

Date of the actual completion of the international search  
31 March 2005

Date of mailing of the international search report  
5 APR 2005

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/AU2005/000191

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
EP	0266149	JP	63109151	US	4873150		
GB	1504577	AT	652775	DE	2444627	DE	2444727
		FR	2285468	FR	2285661	SE	7509418
		US	4263046				
GB	1504547	DE	2456781	FR	2292543	SE	7513386
CA	2149010						

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX